

AN INTEGRATED APPROACH TO MINIMIZING GYPSUM AND PYRITE WASTES BY CONVERSION TO MARKETABLE PRODUCTS

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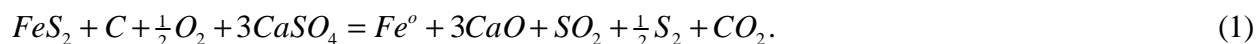
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ABSTRACT

U.S. coal burning utilities and coal mining industry produce tens of millions of tons of gypsum(CaSO_4) wastes as post-combustion flue gas desulfurization (FGD) by product and pyrite(FeS_2)-containing tailings of pre-combustion coal cleaning processes. These two major sources of voluminous wastes are currently disposed of by impoundment. Gypsum and pyrite wastes thus disposed not only occupies thousands of acres of land but also create serious land and water pollution problems due to release of hazardous substances such as heavy metals and acid as a result of weathering and chemical decomposition.

The present study is aimed to develop an innovative technique for combined disposal of gypsum and pyrite wastes. In the proposed process gypsum and pyrite will be utilized to produce lime, iron, and sulfur via a novel chemical process. This process primarily consists of three subsequent stages. The first is the thermal decomposition of pyrite into pyrrhotite and sulfur. This is followed by the reduction of pyrrhotite with carbon in the presence of lime to produce iron and calcium sulfide. The third step involves the reaction of calcium sulfide with gypsum to produce lime (the Muller Kuhne reaction). The overall reaction is:



Lime produced from this process can be fed back to the flue gas scrubber and directly reduced iron (DRI), concentrated SO_2 , and elemental sulfur are salable products. The proposed process will be able to convert gypsum and pyrite wastes to economically viable resources for production of sulfur and iron products and simultaneously produce lime needed for flue gas scrubbing to remove SO_2 from coal combustion.

Enhanced gravity separation tests using Falcon Concentrator and flotation tests have shown that pyrite can be upgraded to 90% with a high recovery. Thermogravimetric analysis (TGA) has shown that pyrite was readily decomposed above 650°C under nonoxidizing conditions, producing the pyrrhotite with a S/Fe ratio of slightly larger than 1. Approximately 42% of sulfur can be removed from pyrite by thermal decomposition. A strong dependence of the reaction rate (k) on temperature (T) was observed for the reaction of pyrrhotite with lime. At

950° C the reaction reached only 70% completion in more than two hours, while at 1050° C 95% completion was reached in 30 minutes. The rate constant of the reaction can be estimated from the slope of the linear part of the reaction rate curve and correlated with the temperature T in Equation (2):

$$\ln k = -35.955 \times 10^3 / T + 28.96. \quad (2)$$

The activation energy was determined to be approximately 299kJ/mol, which is in excellent agreement with the result of 308 kJ/mol published by others.

The effect of surface area on the rate of reaction of mixtures was investigated with different FeS:CaO:C mole ratios at 1000° C. The results have shown that the lime content in the initial mixture had more significant effects on the rate of the reaction than carbon content. The 50% completion time was decreased from 20 minutes to 15 and 10 minutes by doubling the initial carbon content and lime content, respectively. Increase in lime content also reduced sulfur content in iron.

The effective separation of the iron product produced in this reaction is necessary for the process to proceed. Magnetic separation was used to separate iron from calcium sulfide due to their difference in magnetic susceptibility. The composition of the separation product depends on the reaction temperature. With the reaction product obtained at 1000° C, magnetic separation produced the magnetic product that recovered 97.5% iron and rejected 86.7% calcium and 88.7% sulfur.

The kinetics of the Muller Kuhne reaction has been studied as a function of temperature. The results indicate that at 1150° C 90% completion was reached in about 20 minutes and slower reaction kinetics was observed at lower temperatures. The reaction rate and the completion extent were only slightly decreased in the presence of CaO. The XRD (X-ray diffraction) analysis has shown that the product mixture consists of CaO and traces of CaSO₄ and CaS. The rate constant k for this reaction can be described in Equation (3):

$$\ln k = -28.697 \times 10^3 / T + 22.25, \quad (3)$$

which results in an activation energy of 239 kJ/mol.

The effect of surface area or relative abundance of CaS and CaSO₄ on the reaction rate was studied at 1050° C. The stoichiometric mixture (with CaS:CaSO₄ =1:3 mole ratio) reached 73% of reaction completion within an hour. The mixture with a 3 time stoichiometric excess of CaS (with CaS:CaSO₄ =1:1 mole ratio) yielded 82% completion at 60 minutes and the mixture with a 2 time stoichiometric excess of CaSO₄ (with CaS:CaSO₄ =1:6 mole ratio) reached 96% completion at the same time. The results indicate that the excess of the reactants, particularly CaSO₄, enhances the degree of reaction completion.